Water management in Ontario

Ontario
Water Resources
Commission

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Ontario

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REPORT ON

AN INDUSTRIAL WASTES SURVEY

OF

CYANAMID OF CANADA, LIMITED

Welland, Ontario

July 1970

Division of Industrial Wastes

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ONTARIO WATER RESOURCES COMMISSION

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REPORT

Ontario Water Resources Commission

Municipality Welland, Ontario. Date of Inspection July 1970.

Re: CYANAMID OF CANADA, LIMITED

Field Inspection by P. Chisholm Report by P. Chisholm

An intensive industrial wastes survey was conducted at Cyanamid of Canada, Limited, Welland Plant during July 1970. This industrial complex, situated on the north bank of the Welland River between the City of Welland and the Niagara River had not been surveyed for several years. The specific objectives of the survey were to determine the volumes and concentrations of wastes discharged from the complex to the Welland River, to calculate, using these figures, the total loading of industrial wastes from the Cyanamid complex to the Welland River, and to determine individual plant contributions to the total loading.

A biological survey of the Welland River upstream and downstream of Cyanamid was carried out in June - July 1964. In that survey, no samples of undiluted Cyanamid wastes were obtained for analysis. As part of this present survey, therefore, samples of the two main discharges from Cyanamid, the main 36" sewer to the Welland River and Thompson's Creek, known locally as Miller's Creek, were obtained and toxicity tests carried out.

Thompson's Creek upstream of Cyanamid has no flow for the most part of the year, and there was no flow at the time of this survey. When net loadings to, and concentrations in, Thompson's Creek are discussed, it should be remembered that, except during rainstorms, the creek is wholly formed by waste discharges from the Cyanamid complex.

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SUMMARY

Cyanamid of Canada, Limited, Welland Plant, is a large complex of separate plants arranged to operate in conjunction with one another to yield a range of nitrogenous products, such as ammonia, urea, ammonium nitrate, dicyandiamide, melamine, guanidine nitrate, picrite, 3 Amino 123 Triazol, xanthates, phosphine and aureomycin mash.

Since late 1968, the Company has routinely sampled and analysed wastes from the two discharges. Results of these analyses have been forwarded to the Commission on a monthly basis, and are shown in Tables 1 and 2 which follow.

TABLE 1

CYANAMID DATA

36" SEWER WASTE LOADING TO WELLAND RIVER

DATE	VOLUME IGPM	AMMONIA NITROGEN TONS/DAY	KJELDAHL NITROGEN TONS/DAY	UREA NITROGEN TONS/DAY	NITRATE NITROGEN TONS/DAY
DEC./68	-	1.03	8.68	4.37	1.02
FEB./69	-	3.50	24.44	8.07	1.37
MARCH/69	-	2.50	14.77	6.89	0.66
APRIL/69	500	1.20	9.60	3.80	0.80
MAY/69	500	0.80	8.20	6.40	0.69
JUNE/69	500	2.37	5.52	3.12	0.87
JULY/69	500	2.80	6.40	3.00	1.30
AUG./69	500	2.80	6.60	3.20	3.00
SEPT./69	500	2.70	5.60	2.70	0.90
OCT./69	500	3.40	6.70	3.10	1.50
NOV./69	500	3.50	6.80	3.10	2.20
DEC./69	500	3.80	6.60	2.70	1.10
JAN./70	500	3.60	6.80	3.10	0.80
FEB./70	500	3.00	6.10	3.00	0.60
MAR./70	500	3.20	6.50	3.10	0.80
APRIL/70	500	2.50	5.10	2.50	0.90
MAY/70	500	2.90	6.10	3.00	1.50
JUNE/70	500	2.20	5.20	2.90	1.10
JULY/70	500	1.20	2.50	1.20	0.48
AUG./70	500	2.50	5.60	2.90	0.83
SEPT./70	500	2.00	5.10	3.00	0.90
OCT./70	500	1.80	3.90	2.10	0.80
NOV./70	500	2.20	6.40	4.00	0.90
DEC./70	680	2.80	5.80	2.70	1.30
JAN./71	600	3.10	7.30	4.10	1.70
FEB./71	513	2.00	5.30	3.10	1.00
MARCH/71	625	2.40	5.30	2.70	1.20

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TABLE 2

CYANAMID DATA

WASTE LOADING TO THOMPSON'S CREEK

DATE	VOLUME IGPM	AMMONIA NITROGEN TONS/DAY	KJELDAHL NITROGEN TONS/DAY	UREA NITROGEN TONS/DAY	NITRATE NITROGEN TONS/DAY
DEC./68	8,615	1.77	22.58	4.65	3.01
FEB./69	7,785	2.92	19.32	3.78	2.65
MAR./69	9,100	2.56	20.83	3.76	5.53
APR./69	9,317	1.70	18.50	3.30	2.60
MAY/69	8,190	2.00	20.50	4.00	2.20
JUNE/69	5,524	2.90	15.90	2.40	1.10
JULY/69	3,600	1.96	6.49	1.00	2.73
AUG./69	5,000	1.85	12.50	1.45	2.17
SEPT/69	5,000	2.70	12.30	1.60	2.00
OCT./69	5,000	2.10	10.20	1.10	1.30
NOV./69	5,750	2.00	12.40	1.20	2.10
NOV./69	6,000	2.40	13.40	1.40	2.30
JAN./70	5,300	2.70	16.20	1.70	2.60
FEB./70	7,125	2.20	16.20	1.40	2.20
MAR./70	7,800	2.70	15.40	1.60	4.50
APR./70	7,290	2.90	15.00	2.40	2.90
MAY/70	5,248	2.50	11.60	1.90	2.40
JUNE/70	5,420	3.00	12.90	2.00	1.50
JULY/70	3,590	1.30	5.38	0.87	0.69
AUG./70	5,000	1.90	8.70	1.50	0.93
SEPT/70	4,666	1.80	8.20	1.40	0.70
OCT./70	4,700	2.10	9.10	1.20	0.90
NOV./70	5,400	2.10	10.10	1.50	1.20
DEC./70	4,910	1.90	9.30	1.50	1.00
JAN./71	4,700	2.30	8.90	1.70	1.40
FEB./71	5,300	2.70	8.40	1.80	2.40
MAR./71	5,900	2.10	9.40	1.50	1.00

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These results indicate that:

(a) Thompson's Creek

the levels of free ammonia and nitrates have remained relatively unchanged while there has been a limited improvement in non-nitrate nitrogen (Kjeldahl nitrogen) and urea discharges.

(b) Main 36" Sewer to Welland River

the levels of free ammonia and nitrates have remained relatively unchanged while there has been a slight improvement in non-nitrate nitrogen (Kjeldahl nitrogen) and urea discharges.

There has been a very limited improvement in the quality of wastes discharged.

Cyanamid's waste treatment programme to date has emphasised housekeeping improvements and in-plant changes to reduce the amounts of contaminants being discharged to the Welland River. The Company has never discussed the possibility of treating the final contaminated waste flow before discharge to the river. Though there has been a slight reduction in the amounts of certain contaminants being discharged, the present quality of these effluents is not acceptable to the Ontario Water Resources Commission. Furthermore, it is not considered possible for the Company to approach Commission objectives by means of in-plant controls alone. Some form of treatment of the final effluent must be considered.

The problem of waste discharges from the Cyanamid complex is complicated by the unusual flow pattern in the Welland River at this point. The last four miles of the river from Chippawa to the Chippawa/Queenston Power Canal flow backwards to supply water to the Queenston Hydro-electric Station.

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Therefore, the Welland River flows in an easterly direction from the City of Welland, and in a westerly direction from Chippawa to meet at the mouth of the Chippawa/Queenston Power Canal. The requirements for water at the hydro station fluctuate greatly. At times of high water demand, more water is drawn from the Niagara River and there is no room for the easterly flow of the Welland River in the hydro canal. Under these conditions, the Welland River backs up and even flows in a westerly direction. This usually occurs twice every 24 hours with the Welland River backing up as far as the City of Welland. The consequences of this flow pattern are:

(1) Cyanamid draws the bulk of its water supply from the Welland River. Therefore, there are times when the Company's water supply is being contaminated by its own discharges. This would account for the high concentrations of ammonia and Kjeldahl nitrogen found in plant cooling waters.

(2) The effects of waste discharges to the Welland River from the Cyanamid complex can be found upstream of the complex. An indication of how much the backward flow of the river, already contaminated by Cyanamid's waste discharges, affects the quality of the river at Cyanamid's water intake can be seen by comparing the analytical results of the afternoon and evening samples of the river at this point.

Sample Number	T 28-16	T 28-54
Time	Afternoon	Evening
pH	8.7	8.1
BOD_5	4.0	4.0
COD	40	15
Kjeldahl Nitrogen	20	9.0
Ammonia Nitrogen	11	3.0
Nitrate Nitrogen	7.6	1.9
Nitrite Nitrogen	1.2	3.6

The afternoon sample, when the river had backed up, contained twice as much Kjeldahl nitrogen, and four times as much free ammonia and nitrates as the evening sample.

The evaluation of toxicity for aquatic organism is based on the use of Tlm or median tolerance limit. This represents the concentration at which half the test organisms will succumb over a given period of exposure such as 24, 48, or 96 hours. It does not, therefore, represent a safe concentration, and a dilution factor is applied to ensure a safe condition, including an allowance for sub-lethal effects.

Results of bio-assays have shown that the 96 hour Tlm values for the Main Mill 36" Sewer and Thompson's Creek are 1.3% and 13% respectively. This means that half the test fish died in 96 hours in a 1.3% solution

of the 36" sewer and a 13% solution of the sample from Thompson's Creek.

Using the equation -

$$\text{Dilution Volume} = \frac{100 - \text{Tlm}\ \%}{\text{Tlm}\ \%} \times \begin{matrix}\text{Effluent Flow} \\ \text{in GPM}\end{matrix}\ ^{(1)}$$

the total dilution required to elevate these waste flows to the median tolerance limit is 74,760 Igpm. It was found, probably due to the presence of urea that the wastes from Cyanamid were persistently toxic, and thus the application factor to allow for sub-lethal effects should be 100.[(1)(2)] Therefore the dilution necessary to render Cyanamid's wastes safe is 7,476,000 Igpm. The combined volume of both main waste discharges from Cyanamid is in the region of 6,000 Igpm. The ratio of total dilution necessary to the volume of wastes discharged is 1250:1. By the same token, if these wastes are to be discharged without treatment, and no dilution were available, the concentration of toxic contaminants must be reduced 1250 times. Such an improvement in final effluent quality does not appear feasible by in-plant controls alone.

There is little assimilative capacity for Cyanamid's wastes in the Welland River. Low dry weather flows, and on occasion no flow at all, are characteristic of the river above Welland. At Welland, the flow is augmented by the diversion of approximately 230 cu. ft./sec. from the Welland Ship Canal. During the summer months the river flow past Cyanamid might be 300 - 350 cu. ft./sec. or 110,000 - 128,000 Igpm. This represents a dilution ratio of 21:1 for Cyanamid wastes.

Upstream of the City of Welland, there are virtually no discharges to the Welland River, and the quality of the river is satisfactory. The

(1) see appended biological report

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(2) "Guidelines and Criteria for Water Quality Management in Ontario"

first major input of wastes to the river occurs at Welland. City wastes receive primary treatment before being discharged to the river. By the end of 1973, however, the Welland Pollution Control Plant will have been expanded and secondary treatment will be in effect. Apart from Cyanamid's discharges, there are several other significant industrial discharges to the Welland River. Without exception, systems to treat wastes from these industries are either at an advanced stage of planning or actually under construction, and these discharges should be under control by 1973. It is likely that by late 1973 only Cyanamid of Canada, Limited will be discharging contaminated wastes to the Welland River.

As previously mentioned, the Cyanamid complex consists of a series of industries arranged to operate in conjunction with one another. The list of plants is ammonia, nitric acid, urea, ammonium nitrate, dicyandiamide, melamine, guanidine nitrate, picrite, neutralization, 3 Amino 123 triazol, aurofac, phosphine and xanthate. There is no manufactured end-product as such from the neutralization plant, however this plant is an integral part of the manufacturing process at Cyanamid, and has therefore been included. All plants operate continuously 24 hours/day, 7 days/week, 50 weeks/year. There is a two-week shutdown maintenance period each summer.

DETAILS OF SURVEY

On April 14, 1970, staff from the Division of Industrial Wastes visited Cyanamid of Canada, Limited, to gather information which would allow an industrial wastes survey of the plant to be carried out. Details of individual plant processes were discussed, and each plant was visited to locate possible sampling points.

On July 7, the plant was revisited. Labelled sample bottles were left at each of the points to be sampled. At this time, there were further discussions with the Company on process description, flow rates etc. to confirm the accuracy of previous discussions.

On July 8, Commission staff returned to take samples. Sampling of the complex lasted from 9:00 a.m. - 10:00 p.m. As all plants within the complex operate continuously on a 24-hour basis, it was deemed that a 12-hour sampling period would provide satisfactory data for this survey.

Sampling and Analysis

Composite sampling over the 12-hour period consisted of two 6-hour composite samples collected at each location. Composite samples were made up by collecting equal aliquots every half-hour into a 40 oz. sampling bottle. Because of the number of analyses required all samples were collected in duplicate.

Composite samples of the following were collected:

(1) Welland River upstream and downstream of the plant, and

(2) Both main discharges from the plant to the Welland River, Thompson's Creek and the main 36" sewer.

Grab and/or composite samples were collected at the individual plants within the complex. Whether grab or composite samples were collected was decided by the severity of the problem at the plant.

Samples were labelled as to time of sampling, name of plant, location of waste flow within the plant, type of sample - grab or composite, and the name of the operator who did the sampling.

All samples were taken to the OWRC Laboratory in Toronto in the early morning of July 9. All samples were checked to ensure correct labelling and were refrigerated. The analytical results obtained from the Laboratory Division are included in this report.

Water Supply and Treatment

The Company uses three separate sources of water, namely the Welland River, private wells and the municipal supply from the City of Niagara Falls. The respective volumes of water from these sources in Imperial gallons per day are 9,000,000, 33,000 and 240,000.

A small portion of the water drawn from the Welland River is used untreated for cooling purposes. However, most of the water from this source is treated prior to use.

Treatment consists of the addition of ferrous sulphate, calcium carbonate and oxygen to the raw water. The addition of these chemicals produces a ferric hydroxide floc which settles to form a sludge bed. The sludge bed acts as a filter on the river water which is naturally high in suspended solids.

Used ferric chloride sludge is automatically pumped to a settling (accelator) pond where solids settle. The supernatant liquid from the pond overflows to Thompson's Creek.

There is a great variation in water consumption at Cyanamid in summer and winter. Ambient and river water temperatures dictate that much more cooling water is used during the summer months.

Personnel Participating

Various Company personnel were interviewed to obtain information on plant processes, production rates and flow rates of wastes etc. The following Company personnel were contacted:

Mr. R. Reid	-	Pollution Co-ordinator
Mr. E. Brady	-	Chemist-in-Charge Laboratories
Mr. E. H. Fisher	-	Superintendent Power Division
Mr. G. Slaney	-	Superintendent Ammonia/Urea Complex
Mr. B. Power	-	Technical Assistant - Xanthate Plant
Mr. H. Mattice	-	General Superintendent - Guanidine Nitrate and 3 AT Plants
Mr. D. Fry	-	Superintendent - Nitric Acid and Ammonium Nitrate Plant
Mr. D. Roy	-	Superintendent - Dicyandiamide and Melamine Plants
Mr. B. Kingston	-	Superintendent - Aurofac Plant

Ontario Water Resources Commission personnel involved in the survey were Mr. P. Chisholm, Mr. J. D. Luyt, and Mr. H. L. Bell.

SUMMARY OF RESULTS

Discharges of ammonia and other forms of nitrogen to the Welland River were the most serious problems noted during the survey. For the purposes of this report it was estimated that 9,810 lbs. of free ammonia, 26,880 lbs. of Kjeldahl nitrogen, which includes ammonia nitrogen and 7,120 lbs. nitrates were discharged daily to the Welland River.

The Company was also found to discharge excessive amounts of COD-exerting materials, suspended solids, dissolved solids, chlorides, sulphates, chromium, nickel, and zinc. Traces of cyanide contamination were also noted. Portions of the Welland River were found to be discoloured by wastes discharged from Cyanamid resulting in aesthetic pollution.

The paramount problem at Cyanamid is the discharge of free ammonia and other forms of nitrogen. The following tables show (a) totals of free

ammonia and other nitrogenous products being discharged to the 36" sewer and to Thompson's Creek and (b) loadings from individual plants with significant free ammonia or nitrogen-rich discharges.

All loadings are expressed in lbs./24-hour period, and are net loadings calculated by subtracting the raw water loading.

TABLE 1

TOTAL CYANAMID DISCHARGES OF NITROGENOUS COMPOUNDS

Source	Flow Igpm	Free Ammonia lbs/day	Kjeldahl Nitrogen lbs/day	Nitrate lbs/day	Nitrite lbs/day
36" Sewer	550	145	10,180	6,990	-
Thompson's Creek	5,500	9,665	16,700	220	-
TOTALS	6,050	9,810	26,880	7,120	

TABLE 2

INDIVIDUAL PLANT DISCHARGES OF NITROGENOUS COMPOUNDS

PLANT	Flow Igpm	Free Ammonia lbs/day	Kjeldahl Nitrogen lbs/day	Nitrate lbs/day	Nitrite lbs/day
Ammonium Nitrate	420	1,050	945	240	-
Neutralization	10	-	5	-	-
Dicyandiamide	2,735	885	20,810	-	260
Main Steam	125	-	-	360	40
Urea	120	2,900	9,420	-	14,200
Nitric Acid Cooling Water	500	-	210	-	-
Ammonia/Urea Cooling Water	250	160	140	115	-
Picrite	300	-	560	-	125
Melamine	10	10	310	60	-
3 AT	300	790	730	-	-
Overflow from Sludge Pond	300	3,180	7,740	1,570	100
TOTALS	5,070	8,975	40,870	2,345	14,725

There are obvious differences in the totals in Tables 1 and 2. These can be attributed to the instability of ammonia, urea and nitrites. Much of the ammonia discharged quickly breaks down to form nitrites and nitrates. Nitrites are soon oxidized to nitrates and urea would be expected to convert to ammonia, though this is a fairly slow conversion. It should also be remembered that sampling of the complex was carried out manually by three persons. Differing sampling techniques will affect results to some degree.

Other loadings from the Cyanamid complex expressed in lbs/24-hour period are shown in Table 3.

TABLE 3

TOTAL PLANT LOADING OF NON-NITROGENOUS CONTAMINANTS

Parameter lbs/day	36" Sewer	Thompson's Creek	TOTAL
BOD_5	Analysis inhibited by interference.	460	-
Suspended Solids	60	2,380	2,440
Dissolved Solids	27,550	34,420	61,970
Sulphates	1,620	12,910	14,530
Chlorides	7,400	6,420	13,820
COD	2,080	5,950	8,030
Chromium	42	Not analysed	-
Nickel	Not Analysed	100	-

Traces of cyanides were found in several discharges.

DISCUSSION OF RESULTS

Each plant within the Cyanamid complex contributes to some extent to the total loading from the complex. All waste loadings in this section are net increases on parameters in the Welland River and are expressed in lbs./24-hour period.

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Plants Discharging to 36" Sewer

The direct discharge to the Welland River via the 36" sewer contains discharges from the urea, ammonia, main steam and ammonia/urea cooling water plants.

The urea plant poses a most severe problem. Almost all the free ammonia, Kjeldahl nitrogen and nitrite discharged to the 36" sewer originates at the urea plant. Samples obtained during the survey indicated that the urea plant discharges 2,900 lbs. free ammonia, 9,420 lbs. Kjeldahl nitrogen and 14,200 lbs. of nitrite each 24 hours. Two waste streams whose total volume is 30 Igpm are responsible for this loading. Before discharge to the sewer this contaminated discharge is diluted by a 90 Igpm cooling water flow.

There are three discharges to the 36" sewer from the ammonia plant. These are the sulphonyl scrubbers overflow, cooling water discharge and the sulphuric acid overflow from the regeneration system. The total volume of all three discharges is 5 - 10 Igpm. Though these contain excessive concentrations of BOD_5, COD, Kjeldahl nitrogen, free ammonia and chromium, the contribution from this plant to the 36" sewer loading is small.

The main steam plant within the complex discharges a constant blowdown of 125 Igpm to the 36" sewer. This discharge contains excessive concentrations of dissolved solids, sulphates, chlorides, COD and nitrates. The pH of this discharge is also high.

The ammonia/urea cooling tower has a constant discharge of 250 Igpm to sewer. A chromate/zinc/phosphate corrosion inhibitor is used and excessive concentrations of metals were found in the discharge. Other characteristics of this flow are high values of dissolved solids, Kjeldahl

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nitrogen, free ammonia, nitrates, COD, sulphates and chlorides. Phosphates were not analysed.

Plants Discharging to Thompson's Creek

The remainder of plants at Cyanamid discharge to Thompson's Creek. Of these, the ones with most serious problems are the dicyandiamide, ammonium nitrate, neutralization and 3 Amino 123 Triazol plants.

Total flow from the dicyandiamide plant via two sewers is in excess of 2,700 Igpm and the loadings to Thompson's Creek are 885 lbs. of free ammonia, 20,810 lbs. of Kjeldahl nitrogen, and 260 lbs. of nitrite. The mother liquor discharged from the dicyandiamide plant contains 14 ppm HCN. Dissolved solids, COD, sulphates and chlorides were all found in excessive concentrations.

The ammonium nitrate plant has two main discharges, the south sewer and control launder discharges, whose respective volumes are 400 Igpm and 20 Igpm. South sewer loadings are 1,040 lbs. free ammonia, 935 lbs. Kjeldahl nitrogen, 185 lbs. nitrates and 580 lbs. dissolved solids. Loadings from the central launder sewer are much less significant, and are more fully discussed later in the report.

There are two waste discharges from the neutralization plant. One flows directly to Thompson's Creek and the other to a sludge settling pond. The major discharge, 300 Igpm, is to the sludge pond. Solids are settled out in the pond and the supernatant liquid overflows to a ditch which leads to Thompson's Creek. Analysis of the overflow showed the daily loading to be 19,850 lbs. dissolved solids, 3,180 lbs. free ammonia, 1,570 lbs. nitrate, 7,120 lbs. sulphate, 7,740 lbs. Kjeldahl nitrogen and 100 lbs. nitrite. The direct discharge to the creek, 10 Igpm, contains suspended

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and dissolved solids, free ammonia, Kjeldahl nitrogen and chemical oxygen demand exerting materials.

The 3 AT (3 Amino 123 Triazol) plant has two waste discharges. Mother liquor, a volume of 9,000 Igpd, is discharged containing 560 lbs. free ammonia, 500 lbs. Kjeldahl nitrogen, 2,000 lbs. dissolved solids and 60 lbs. COD exerting materials. The second discharge, 80 Igpm of cooling water, contained 230 lbs. free ammonia and 230 lbs. Kjeldahl nitrogen. Though a nickel analysis was not carried out on these discharges, the nickel shown to be present in Thompson's Creek is thought to originate at the 3 AT plant.

Of the remaining plants, those manufacturing picrite,melamine and xanthates have the most serious problems. The picrite plant has a 300 Igpm waste flow discharging 3,640 lbs. dissolved solids, 580 lbs. Kjeldahl nitrogen, 105 lbs. nitrate and 100 lbs. COD exerting materials. Discharges from the melamine plant contain daily loadings of 275 lbs. Kjeldahl nitrogen, 205 lbs. dissolved solids, 50 lbs. suspended solids and 50 lbs. nitrates.

During the survey, discharges from the xanthate plant were found to be extremely high in BOD_5. An application to change the xanthate process has been received by the Commission. The proposed change would eliminate these high BOD_5 wastes. There is evidence that xanthates are being flushed to the sewer during wash-up procedures.

Other plants discharging to Thompson's Creek are nitric acid, guanidine nitrate, aurofac and phosphine. Discharges from these plants are of a comparatively minor nature and are dealt with more fully in the individual plant summaries.

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In summary, five plants are responsible for most of the free ammonia and Kjeldahl nitrogen discharged from the Cyanamid complex. These are the urea plant, discharging directly to the Welland River via the 36" sewer, and the dicyandiamide, ammonium nitrate, neutralization and 3 AT plants, discharging to Thompson's Creek. However, all remaining plants within the complex have lesser discharges containing excessive amounts of free ammonia and/or Kjeldahl nitrogen.

The ammonia/urea cooling water plant discharges quantities of the heavy metals chromium and zinc. A cooling water discharge from the ammonia plant contained high concentrations of chromium. The nickel found in Thompson's Creek is thought to originate at the 3 AT plant where a nickel/chromium catalyst is used.

High BOD_5 and COD exerting wastes are discharged from the xanthate plant though plans have been received to eliminate these discharges. Xanthates are washed to sewer during normal clean-up operations.

Samples obtained during this survey were not "fixed" with sodium hydroxide so full cyanide analyses could not be carried out. Nonetheless some cyanide analyses were conducted. The sample of Thompson's Creek used for bioassays contained 0.3 ppm HCN and the mother liquor discharge from the dicyandiamide plant contained 14 ppm HCN. As some breakdown of these cyanides would have occurred before analysis, these figures must be regarded as being lower than is actually present. Further sampling of the complex, with cyanide analysis in view will be carried out.

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Traces of phosphates were found in several discharges. However, phosphates were not generally analysed during this survey.

EFFECTS OF CONTAMINANTS

Free Ammonia and Nitrogenous Compounds

Free ammonia is undesirable in surface waters because it is toxic to fish, exerts a high oxygen demand when it is converted to nitrite and nitrate, and is a source of nitrogen for plants which can help promote excessive algal growth. It is rarely found in concentrations high enough to be harmful to humans. Organic nitrogen, nitrites, and nitrates are sources of nitrogen which may promote excessive algal growth. Except for nitrates they also exert high oxygen demand.

The total Kjeldahl nitrogen analysis measures the sum of organic nitrogen and free ammonia in the sample but not nitrates and nitrites.

Heavy Metals

Heavy metals cannot be assimilated, but are retained by and accumulated in the environment.

Chromium salts have little effect on fish at concentrations of 1 ppm. Lower forms of aquatic life are, however, affected by a fraction of a part per million. It must be remembered that the toxicity of chromium salts towards aquatic life varies widely with species, temperature and pH.

Zinc and zinc salts are toxic to fish and lower forms of aquatic life. Irrigation water containing zinc may have an adverse effect on crops.

Nickel is less toxic than zinc and chromium to fish and lower forms of aquatic life. However, irrigation waters containing nickel can cause injury to plants no matter how small the quantity of nickel.

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Xanthates

The extremely toxic nature of some xanthates to fish and other forms of aquatic life is being investigated, but indications are that the 96-hour Tlm is in the region of 1 ppm. Assuming an application factor of 100 for this type of product, a maximum safe concentration of 0.01 ppm in Thompson's Creek is desired.

Cyanides

Cyanides are extremely toxic to fish but less so to the lower aquatic organisms. Certain metals form cyanide complexes. The nickel cyanide complex reduces the toxicity of the cyanide. On the other hand zinc and cadmium cyanide complexes are much more toxic than the cyanide itself.

Cyanides are generally soluble in water, dissociating to the CN^- which combines with hydrogen ions to form weakly dissociated hydrogen cyanide. It is the hydrogen cyanide that exhibits extreme toxicity and not the cyanide ion.

Phosphates

Phosphates themselves seldom exhibit toxic effects upon fish and other aquatic life, and may have a beneficial effect by increasing algae and zooplankton. However, excessive discharges of phosphates to streams or lakes, especially in the presence of nitrogenous compounds, may result in an over-abundance of algae with resultant odours and a reduction of oxygen available to fish.

Biology Report

The complete biological report is attached to this report.

In summary, 96-hour Tlms for the 36" sewer and Thompson's Creek were 1.3% and 13% respectively. The dilution required to produce a

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safe concentration of these wastes is approximately 7.5 million Igpm. It should be remembered that tap water containing no free ammonia was used for dilution at the Commission Laboratories. Using Welland River water, which contains free ammonia, the amount of water required to produce a safe concentration of wastes would be greater than the 7.5 million IgpM figure.

Staff at the Biology Branch have stated that Cyanamid's wastes were as toxic as any they have been asked to test.

It is normal in bioassays that the test solution becomes less toxic as the test proceeds. This did not occur with Cyanamid's discharges. The test solutions were more toxic after 2 - 3 days than they had been when the test was started. This can be attributed to breakdown of urea in the test solutions liberating more ammonia to the test solutions.

CONCLUSIONS

Based on the findings of this survey, it was estimated that the net daily free ammonia, Kjeldahl nitrogen and nitrate loadings to the Welland River from Cyanamid of Canada, Limited, were in the order of 9,810 lbs., 26,880 lbs. and 7,120 lbs. respectively.

It should be remembered that these net figures are based on concentrations of free ammonia, Kjeldahl nitrogen and nitrate in the Welland River at Cyanamid's water intake, and that these raw water samples contained unusually high values of Kjeldahl nitrogen, free ammonia and nitrate. The high values must be attributed to Cyanamid's waste discharges being carried upstream by the backward flow of the river. If Welland River samples had been obtained outside the sphere of influence of Cyanamid's wastes; they would be expected to contain much less free ammonia, Kjeldahl

and nitrate with a consequent increase in net loading figures from the complex.

Samples of the Welland River were obtained at the Montrose Road bridge, two miles downstream from Cyanamid. The effects of Cyanamid's waste discharges in terms of concentrations are an increase of free ammonia from 7.0 ppm to 22.0 ppm and Kjeldahl from 14.5 to 41 ppm as opposed to the Welland River at Cyanamid's water intake.

Calculations based on the 96-hour Tlm figures for both waste discharges have shown that a dilution of 7.48 million Igp~~d~~M would be needed to achieve safe concentrations if the above loadings were to be discharged without treatment. This represents a dilution ratio of 1250:1. Therefore, if these wastes were discharged where no dilution was available the loading figures would have to be reduced 1,250 times. The loading would then be 8 lbs. free ammonia, 22 lbs. Kjeldahl nitrogen and 6 lbs. nitrate. The estimated summer flow of 125,000 Igpm in the Welland River would dilute Cyanamid's waste flows 21 times. Therefore, the maximum daily loadings available to Cyanamid that will be safely assimilated in the Welland River are in the order of 170 lbs. free ammonia, 460 lbs. Kjeldahl nitrogen and 125 lbs. nitrates.

Based on the results of other analyses carried out on Cyanamid waste discharges, it was estimated that 2,440 lbs. suspended solids, 61,970 lbs. dissolved solids, 14,530 lbs. sulphates, 13,820.lbs. chlorides and 8,030 lbs. chemical oxygen demand exerting materials are discharged daily to the Welland River.

The heavy metals zinc, chromium and nickel, some cyanides and phosphates are discharged. Accurate estimates of daily loadings of these contaminants are not known.

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Portions of the Welland River were found to be discoloured by wastes discharged from Cyanamid resulting in aesthetic pollution.

The standard of housekeeping at several plants within the complex was not high. There was evidence that spilled products were being flushed to the sewer.

RECOMMENDATIONS

Based on improvements in the quality of Cyanamid's waste discharges to date, the Company must accelerate its efforts to bring these discharges under control. The Company should embark on a staged programme to bring the quality of its waste discharges within Ontario Water Resources Commission objectives. Such a programme might involve:

(1) determing problem areas at each plant within the Cyanamid complex.

(2) segregation of uncontaminated cooling waters from the remaining contaminated wastes and collection of the contaminated wastes.

(3) designing a treatment system for these contaminated wastes. The treatment of nitrogenous wastes containing free ammonia will probably involve either steam stripping, ion exchange and/or biological degradation.

The Company should continue with its programme of in-plant controls as there are many locations within the Cyanamid complex where stricter controls will greatly reduce the total waste loading. Especially important, in this respect, is housekeeping. It is recommended that in-plant housekeeping be improved to attempt to reduce chemical losses to sewer.

The Company should undertake a much more comprehensive monitoring programme than exists at present. All sources of contaminated wastes should be monitored and the analytical results forwarded to the Commission on a monthly basis.

The water flow in the Queenston/Chippawa Power Canal is in the region of 7.5 million Igpm. This is the dilution necessary to safely assimilate the total untreated Cyanamid waste flow. The Company might enter into negotiations with Hydro to explore the possibility of discharging the whole Cyanamid waste flow to the power canal on an interim basis until such time as these wastes are of satisfactory quality for discharge to the Welland River. If this could be arranged, there would be an immediate improvement in the quality of the Welland River between Cyanamid of Canada, Limited, and the power canal, and this area of the river could be more fully developed for recreational purposes.

AMMONIA PLANT

Raw Materials and Products

Ammonia is manufactured from natural gas and water.

Process

Natural gas is mixed with steam, desulphurized by passing it over carbon pellets, and compressed. This mixture is then reformed over a solid manganese oxide catalyst to carbon monoxide and hydrogen gases. Hot air is added and the mixture of carbon monoxide, hydrogen and nitrogen (from the air) is passed through a secondary reformer. The gaseous mixture, at this point, consists of carbon dioxide, nitrogen and hydrogen. This mixture is bubbled through a sulphonyl solution to absorb the carbon dioxide. The remaining hydrogen and nitrogen pass into a reactor where ammonia is formed. The reaction gases are cooled, compressed and the ammonia separated.

$$\text{methane} + \text{steam} \xrightarrow[\text{carbon pellets}]{\text{desulphurized}} \text{compressed} \xrightarrow[\text{Mn oxide}]{\text{primary reformer}}$$

$$CO + H_2 \xrightarrow[\text{steam}]{\text{secondary reformer}} CO_2 + H_2 + N_2 \xrightarrow[\text{sulphonyl scrubber}]{-\ CO_2} H_2 + N_2$$

$$\xrightarrow{\text{reactor}} NH_3$$

This plant operates 24 hours per day, 7 days per week and employs 20 people. Full plant capacity is 700 tons of ammonia per day.

Sources of Liquid Wastes

There is a small, though constant, overflow from the sulphonyl scrubbers to the 36" sewer which leads to the the Welland River. The

volume of the overflow is not known. This sulphonyl solution is a mixture of sulpholane, diisopropylamine and water.

Water softeners are regenerated on a regular basis, at least once per 24-hour period. Two hundred and twenty (220) lbs. of flake sodium hydroxide and 800 lbs. of 60 Baumé sulphuric acid are used in each regeneration. The excess sulphuric acid from this operation is pumped to a storage tank and trickled to the 36" sewer over a 24-hour period. This discharge has been approved by the Ontario Water Resources Commission.

Sludge from the sulphonyl scrubbers is drummed and buried on Company land.

There were two small discharges of cooling water to a ditch adjacent to the ammonia plant. Their total flow was estimated to be 2 gallons/minute.

Sampling and Analysis

On July 8, grab samples of the cooling water discharge to the ditch and the sulphonyl solution and sulphuric acid discharges to the 36" sewer were obtained.

Overflow from Sulphonyl Scrubbers

			Solids				Nitrogen		
Lab No.	Flow	BOD_5	Total	Susp.	Diss.	COD	Total Kjeldahl	Free Ammonia	pH
T28-5	-	75	30	5	25	2,300	120	80	8.7

Cooling Water Bleed-off to Ditch

			Solids			Nitrogen				
Lab. No.	Flow	BOD_5	Total	Susp.	Diss.	Total Kjeldahl	Free Ammonia	NO_3	NO_2	Chromium
T28-55	2 gpm	18	830	25	805	37	29	0.49	7.0	9.7

Sulphuric Acid Overflow to Sewer

Lab No.	Flow	pH	Acidity as $CaCO_3$	Total Kjeldahl Nitrogen
T28-56	-	0.7	37,800	90

DISCUSSION OF RESULTS

All three waste flows are small in volume. Therefore, no waste loadings have been calculated and the overall comments are in general terms.

The sulphonyl scrubber overflow has excessive concentrations of biochemical oxygen demand, chemical oxygen demand, Kjeldahl nitrogen and free ammonia and should not be discharged to a watercourse without treatment.

The cooling water discharge, bright orange in colour, contains high concentrations of chromium and must not be discharged to a watercourse. The problem of corrosion inhibitors in cooling water is discussed elsewhere in this report.

Ontario Water Resources Commission approval has been given for the discharge of spent sulphuric acid from the demineralizing units in the ammonia plant. The approval was based on the fact that a discharge of

such low pH would help neutralize high pH discharges from the urea plant which discharge to the same sewer. However, this present analysis has shown the sulphuric acid overflow to contain excessive Kjeldahl nitrogen. The original OWRC approval of this discharge must now be reconsidered.

NITRIC ACID PLANT

Raw Materials

The raw materials are ammonia, air, and water.

Process

The main reaction equations are:

Reaction 1 - $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

Reaction 2 - $2NO + O_2 \longrightarrow 2NO_2$

Reaction 3 - $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

Overall Reaction: $4NH_3 + 7O_2 \longrightarrow \frac{8}{3} HNO_3 + \frac{4}{3} NO + \frac{14}{3} H_2O$

Ammonia gas is oxidized with air to nitric oxide, reaction 1, in a converter at 900°C using a platimum gauze as catalyst. The nitric oxide and excess air are cooled in a waste heat boiler and a water cooler (indirect cooling) where reaction 2 occurs. The gas is conducted to the bottom of seven water absorption towers arranged in parallel. Six towers have a capacity of 50 tons product per day while the seventh has a capacity of 200 tons per day. The product, nitric acid, is drawn from the bottom. Waste gases from the top of the towers containing nitrogen, oxygen, nitrogen oxides, and water vapour are passed through a power recovery turbine and exhausted to the atmosphere.

The product, nitric acid, is sold as such and also used as a raw material in ammonium nitrate production.

The plant operates on a continuous basis and has a capacity of 500 tons of acid per day.

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Sources of Wastewater

External cooling water is used in the absorption towers. The water is recirculated through a large cooling tower. Small nitric acid purges from each tower to prevent chloride build-up in the acid are directed to limestone-filled neutralization pits before being discharged to sewer. All wastewater flows from the nitric acid plant and drain to Thompson's Creek.

Sampling and Analysis

Grab samples of the nitric acid plant cooling water and of the combined boiler blowdown and acid purge estimated at 1 gpm were taken.

SAMPLE NO.	DESCRIPTION	BOD_5	SOLIDS SUSP.	SOLIDS DISS.	pH	KJELDAHL NITROGEN as N	CHLORIDES as Cl	SULPHATES as SO_4
T28-46	Boiler blowdown limestone pit effluent	4.5	40	900	9.3	29	139	225
T28-47	Cooling water	6.0	10	350	6.3	44	62	79

DISCUSSION OF RESULTS

The cooling water flow, 500 Imperial gallons per minute, discharges 480 lbs. dissolved solids, 210 lbs. Kjeldahl nitrogen, 260 lbs. of sulphates and 225 lbs. of chlorides each day to Thompson's Creek.

There is a sewer discharge from the limestone neutralizing pits. This was estimated at a volume of 1 Imperial gallon per minute. Due to the small volume of this discharge, waste loading figures have not been calculated. These wastes, however, contain excessive amounts of suspended and dissolved solids and Kjeldahl nitrogen.

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UREA PLANT

Raw Materials and Products

Ammonia and carbon dioxide are reacted to form urea and water.

Process

Liquid ammonia and gaseous carbon dioxide are reacted in an autoclave, under conditions of high temperature (185°C) and pressure (3,580 - 3,820 lbs/sq. in.). Reaction is not complete between the ammonia and carbon dioxide and the autoclave discharge contains urea, ammonia and carbon dioxide. The carbon dioxide is exhausted to the atmosphere. The urea/ammonia mixture is cooled and passed to a separating vessel. The urea and ammonia solutions separate with the urea on the surface. The urea is drawn off to be crystallized and the ammonia solution, still containing some urea, is pumped to a second separating vessel. There is a further separation of urea and ammonia solution. The urea again being drawn off to the crystallizer while the ammonia solution is pumped to an ammonia storage tank. The ammonia liquor is then neutralized with nitric acid to ammonium nitrate solution which is pumped to the ammonium nitrate plant.

The liquid urea is pumped to a vacuum crystallizer and the urea crystals are transported to the top of the prill tower. The crystalline urea is melted on hot water pipes and the molten urea falls down the prill tower where it meets an upward current of air forming urea prills, the finished product.

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Reaction Equation

$$2NH_4OH + CO_2 \xrightarrow[\substack{3,580 - 3,820 \\ \text{lbs/sq. in.}}]{185^{\circ}C} CO\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix} + 3H_2O$$

The plant operates continuously 24 hours per day, 7 days per week. The greatest proportion of urea manufactured is sold as such. Some is used as a raw material in other manufacturing processes.

There are three waste streams from the urea plant. All flow to the 36" sewer which discharges directly to the Welland River. There is:

(a) a constant overflow of highly contaminated wastes from the ammonia liquor neutralization unit. This was estimated at 20 gpm,

(b) a constant flow of contaminated crystallizer condensate from the urea crystallizer, estimated at 10 gpm, and

(c) a constant flow of uncontaminated steam condensate from the prill tower, estimated at 85 gpm.

The Company has plans for treating waste flow (a) by means of a "scrubbing" unit. This was to have been in operation by late 1970.

Housekeeping in the urea plant was generally poor. We have now visited the plant four times and on each occasion there was a great deal of urea lying on the floor of the building. This would eventually be hosed to the 36" sewer.

Sampling and Analysis

Two 6-hour composite samples were obtained of:

(a) discharge from ammonia liquor neutralization unit

(b) discharge of crystallizer condensate

(c) total plant effluent to 36" sewer

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Discharge from Ammonia Liquor Neutralization Unit

LAB.NO.	FLOW GPM	BOD	SOLIDS TOTAL	SOLIDS SUSP.	SOLIDS DISS.	COD	CL^-	SO_4^{--}	PH	NITROGEN TOTAL KJELDAHL	NITROGEN FREE AMMONIA	NITROGEN NITRATE	NITROGEN NITRITE
T28-39	20	19	39,000	10	38,990	30	TRACE	2	1-2	8,300	8,100	0.5	3,000
T28-40	20	10	28,700	5	28,695	30	13	9	9-0	9,000	8,100	0.25	9,000

Discharge of Crystallizer Effluent

LAB.NO.	FLOW GPM	BOD	SOLIDS TOTAL	SOLIDS SUSP.	SOLIDS DISS.	COD	CL^-	SO_4^{--}	PH	NITROGEN TOTAL KJELDAHL	NITROGEN FREE AMMONIA	NITROGEN NITRATE	NITROGEN NITRITE
T28-49	20	**	20	5	15	55	9	1	10.0	22,000	21,000	15.2	0.8
T28-50	20	**	15	5	10	40	7	1	9.9	13,000	750	3.6	0.4

Total Plant Effluent to 36" Sewer

LAB.NO.	FLOW GPM	BOD	SOLIDS TOTAL	SOLIDS SUSP.	SOLIDS DISS.	COD	CL^-	SO_4^{--}	PH	NITROGEN TOTAL KJELDAHL	NITROGEN FREE AMMONIA	NITROGEN NITRATE	NITROGEN NITRITE
T28-37	120	13	7,920	40	7,880	55	26	49	9.4	7,000	1,500	0.50	2,300
T28-38	120	16	5,100	15	5,085	45	27	43	9.4	3,800	1,250	0.60	2,650

All results reported in ppm except pH

** indicates interference inhibited analysis

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DISCUSSION OF RESULTS

Three waste streams contribute to the total waste discharge from the urea plant. These are the discharge from the ammonia neutralization unit, the discharge from the urea crystallization unit and steam condensate from the prill tower. These three flows come together in one sewer and are discharged to the 36" sewer which flows to the Welland River. The crystallizer and neutralizer effluents are highly contaminated while the steam condensate from the prill tower is clean water.

The total waste discharge contains high concentrations of dissolved solids, Kjeldahl nitrogen, nitrates, nitrites and free ammonia.

The waste loading from this flow appears in the following table.

Contaminants	Loading in lbs/24-hour Period
Kjeldahl nitrogen	9,160
Free ammonia	5,100
Nitrates	400
Nitrites	13,800
Dissolved solids	10,520
COD	85

Discharges of free ammonia and other sources of nitrogen will be discussed in a separate section of this report.

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AMMONIUM NITRATE PLANT

Raw Materials and Products

Gaseous ammonia reacts with aqueous nitric acid to form ammonium nitrate solution.

Process

The reaction equation is:

$$\underset{\text{Aqueous}}{HNO_3} + \underset{\text{Gaseous}}{NH_3} \xrightarrow{146^{\circ}C} \underset{87\%\ \text{solution}}{NH_4NO_3}$$

Ammonia and nitric acid react in one of three neutralizers at 146°C to form an 87% solution of ammonium nitrate. This solution passes from the neutralizer to one of three evaporating tanks, heated by steam coils, where its concentration is increased to 95% ammonium nitrate. The ammonium nitrate solution is now called strong liquor and passes to the strong liquor storage tank.

The strong liquor is pumped to the top of one prill tower and sprayed through an upward flow of air to form ammonium nitrate prills. The prills are then dried and cooled.

The ammonium nitrate at this stage is used as a raw material in the guanidine nitrate process. If, however, the ammonium nitrate is to be shipped as a finished product for fertilizer use, the prills are blended with clay as coating agent, and bagged for sale.

The plant operates 24 hours per day, 7 days per week. At full capacity the plant manufactures 485 tons of prills per day, or 500 tons of ammonium nitrate strong liquor.

Air discharges from emission towers and cyclones are controlled by water scrubbers. The water from these systems flows to a common closed

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system called the weak liquor system where weak liquor is evaporated. The concentrated liquor left after evaporation is bled back into the manufacturing process.

Sources of Liquid Wastes and Disposal

All waste discharges from the ammonium nitrate plant flow to sewers which lead to Thompson's Creek.

There are three sources of waste waters at this plant, the north ditch, the central launder, and the south sewer.

North Ditch

The north ditch receives only storm run-off from the rail loading area. Most of the loading area is covered. However, some product could at times be washed into the ditch from the uncovered area. During the survey, there was no flow in the ditch.

Central Launder

The central launder runs through the centre of the plant and receives floor and equipment washdown water.

South Sewer

The south sewer is the main sewer for the plant. Continuous flow and conductivity meters have been installed on the sewer. Gas from the neutralizer is water-scrubbed and the water containing ammonia, nitric acid and ammonium nitrate is discharged to sewer. Cooling water is used in barometric condensors on the evaporators. The sewer also serves the prilling tower, predryer, dryer, and prill cooling areas.

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Sampling and Analysis

Sample No.	Description of Samples			Flow (gpm)
T28-9	North Ditch	Grab	11:40 a.m.	Stagnant
T28-7	Central Launder	Composite	10:00 a.m. - 3:30 p.m.	10 - 20
T28-8	Central Launder	Composite	4:30 p.m. - 10:00 p.m.	
T28-29	South Sewer	Composite	10:00 a.m. - 3:30 p.m.	400
T28-30	South Sewer	Composite	4:30 p.m. - 10:00 p.m.	

SAMPLE NO.	BOD_5	SUSP. SOLIDS	DISS. SOLIDS	PH	AMMONIA AS N	KJELDAHL NITROGEN AS N	NITRATE AS N	COD
T28-9	20	60	16,240	7.7	2,400	3,600	1,100	350
T28-7	5	10	280	8.7	13	23	31	45
T28-8	9	20	420	7.9	45	50	52	40
T28-29	13	15	375	9.3	97.5	130	9.9	35
T28-30	7	15	405	9.6	215	220	14.0	30

DISCUSSION OF RESULTS

The south sewer has the largest and most contaminated waste discharge. The flow was estimated at 400 Imperial gallons per minute and the waste loadings from this source over a 24-hour period were 580 lbs. dissolved solids, 1,040 lbs. free ammonia, 935 lbs. Kjeldahl nitrogen and 185 lbs. of nitrates.

The central launder sewer has a flow of 20 Imperial gallons per minute and has a waste loading of 8 lbs. Kjeldahl nitrogen, 10 lbs. free ammonia and 53 lbs. of nitrate in a 24-hour production period.

The general standard of housekeeping was not high at this plant. An indication of this is seen in the results of the sample taken from the

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north ditch. The analysis of the sample taken from the stagnant ditch gave 2,400 ppm ammonia nitrogen, 3,600 ppm Kjeldahl nitrogen, 1,100 ppm nitrate nitrogen, 350 ppm chemical oxygen demand, 60 ppm suspended solids and 16,240 ppm dissolved solids. This ditch is adjacent to the rail loading area. These highly contaminated wastes will be washed to Thompson's Creek by the first heavy rain storm.

DICYANDIAMIDE PLANT

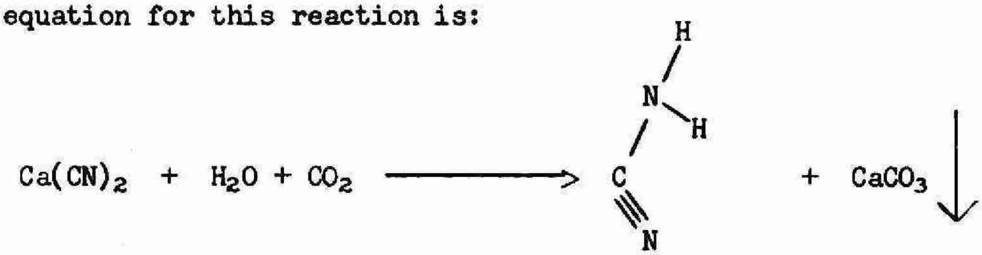
Raw Materials and Products

Calcium cyanide, water and carbon dioxide react to form hydrogen cyanamide and calcium carbonate. The hydrogen cyanamide, under controlled conditions of pH and temperature, polymerises to dicyandiamide.

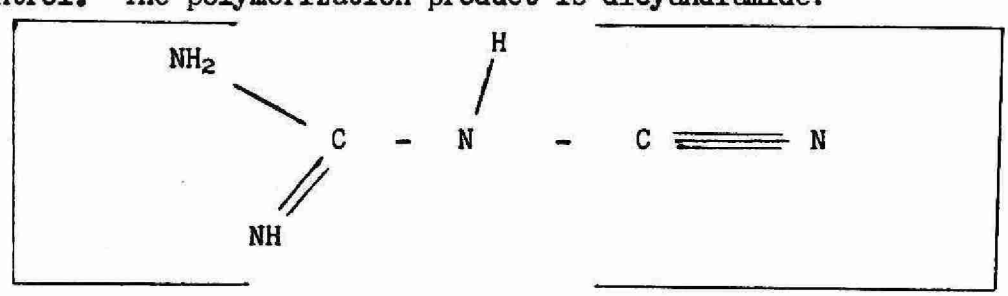
Process

Calcium cyanide is slurried in water and reacted with carbon dioxide to form the cyanamide.

The equation for this reaction is:



The calcium carbonate precipitate is filtered, and the cake amounting to some 400 tons per day is repulped and pumped to the neutralization plant. After filtration, the clear liquor is heated and pumped to one of 6 vacuum converter-crystallizers where the cyanamide is polymerized and crystallized under temperature and pH control. Sodium hydroxide is added for pH control. The polymerization product is dicyandiamide:



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Some urea, melamine and thio urea also form during the reaction. The liquor is then sent to one of two automatic batch centrifuges. A portion of the mother liquor is used to wash the filter cake and this is discharged with the calcium carbonate slurry to the sludge ponds. The remainder is sewered. The wet cake from the centrifuge is passed to one of three rotary drum dryers and the dryed dicyandiamide sent to storage bins for subsequent bulk loading and bagging.

150 - 160 tons of dicyandiamide are produced per day. The bulk of the dicyandiamide manufactured is sold as such but some is used in the manufacture of melamine and guanidine nitrate.

Sources of Liquid Wastes

The "Di-cy" plant is served by sewers draining to Thompson's Creek. The strongest waste at the "Di-cy" plant is the mother liquor discharged directly to the west sewer. Calcium carbonate sludge is pumped from the north and south sumps to the neutralization plant before pumping to the sludge ponds. Overflows from these sumps to plant sewers can and do occur.

Large quantities of dicyandiamide were observed on plant floors and although most is recovered by dry recovery methods, it was apparent that a significant amount would be lost to the sewers during plant wash-downs.

An additional major wastewater flow was the cooling water used in the inter-coolers on the crystallizer vacuum system. This flow was discharged through the west sewer.

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Sampling and Analysis

The following samples were taken:

SAMPLE NO.	DESCRIPTION
T 28-65	Mother Liquor to Sewer - Aliquots - 9:30 a.m., 3:30 p.m., and 8:00 p.m.
T 28-66	West Sewer - Composite - 9:30 a.m. - 3:30 p.m.
T 28-67	West Sewer - Composite - 4:30 p.m. - 6:00 p.m.
T 28-68	South Sump to Neutralizing Station - Comp. 9:00 a.m. - 3:30 p.m.
T 28-57	South Sump to Neutralizing Station - Comp. 4:30 p.m. - 10:00 p.m.
T 28-58	North Sump to Neutralizing Station - Comp. 9:30 a.m. - 3:30 p.m.
T 28-59	North Sump to Neutralizing Station - Comp. 4:30 p.m. - 10:00 p.m.

SAMPLE NO.	SUSP. SOLIDS	DISS. SOLIDS	PH	COD	KJELDAHL NITROGEN AS N	AMMONIA NITROGEN AS N	CHLORIDE AS CL	CYANIDE AS CN^-	SULPHATES AS SO_4
T28-65	5	44935	10.5	9500	16000	-	1564	14	52
T28-66	20	560	9.2	35	600	36.5	110	0.1	42
T28-67	30	300	8.8	40	85	15	57	0.1	158
T28-68	4840	5760	8.6	1440	4800	33	160	1.6	59
T28-57	145	625	8.8	95	19	150	115	-	56
T28-58	1300	1000	8.6	500	65	470	239	-	28
T28-59	280	450	7.5	180	18	65	78	-	56

DISCUSSION OF RESULTS

There are two continuous discharges from this plant. These are the mother liquor discharge, 33 gpm, and the west sewer discharge, 2700 gpm. The respective waste loading from each of these sources is as follows:

(a) Mother Liquor

Contaminants	Discharge per 24-hour period, in lbs.
Dissolved Solids	22,200
Chemical Oxygen Demand	4,770
Kjeldahl Nitrogen	7,990
Sulphates	25
Chlorides	780
Cyanide as HCN	7

(b) West Sewer Discharge

Contaminants	Discharge per 24-hour period, in lbs.
Dissolved Solids	5,750
Chemical Oxygen Demand	390
Kjeldahl Nitrogen	12,820
Free Ammonia	885
Nitrite	260
Sulphates	2,225
Chlorides	2,050

The most serious problem, that of free ammonia and nitrogen discharge, will be discussed in this report.

The mother liquor discharge contained 14 ppm cyanide as hydrogen cyanide, equivalent to a 24-hour waste loading of 7 lbs. of hydrogen cyanide.

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Housekeeping must be improved. Large quantities of finished product were observed on plant floors, some of which has to be washed to the sewer.

MELAMINE PLANT

Raw Materials and Products

Dicyandiamide is autoclaved under pressure in the presence of ammonia to form melamine:

$$\left[N{:}C(HN_2)N{:}C(NH_2)N{:}C(NH_2) \right]$$

Process

Dicyandiamide is fed into a blender, heated to 130°C and sent to one of 5 oil-cooled autoclaves.

In the autoclaves and in the presence of pressurized ammonia the dicyandiamide is converted to crude melamine. The melamine is removed from the autoclaves by a drill rig and fed to a pulverizer and premix tank where activated carbon is added. The mixture is fed into a crude slurry tank where water is added until a slurry containing 10% solids is formed. The slurry temperature is raised to 130°C to dissolve the melamine and the solution is filtered by a pressure leaf filter. The filter cake is conveyed to the Company's dump. The filtrate is conveyed to one of three crystallizers to form a crystal slurry containing 35% solids. This is fed to a Sharples continuous centrifuge. In the centrifuge, the crystal slurry is water washed with the separated water returning to the crystallizer. The crystallizer mother liquor is sent to a mother liquor storage tank and added to the premix tank to form the melamine slurry. The refined melamine crystals removed from the slurry are fed to the centrifuge, dryed in a steam-jacketed

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rotating screw dryer, pulverized and bagged for sale.

Sources of Liquid Wastes and Disposal

All wastewater from the melamine plant is discharged to plant sewers emptying into Thompson's Creek. Once-through indirect cooling water is used to cool the recirculating oil used in the autoclaves. A 500-gallon per shift purge of mother liquor is sewered. Other waste waters include floor and equipment washdown water. There were substantial quantities of powder on plant floors during the day of the survey.

Sampling and Analysis

Sample No.	Description	Flow (gpm)
T 28-41	Mother Liquor Purge	1
T 28-42	Main Plant Sewer Composite - 9:00 a.m. - 3:30 p.m.	10
T 28-43	Main Plant Sewer Composite - 4:30 p.m. - 10:00 p.m.	10

SAMPLE NO.	BOD_5	COD	SUSP. SOLIDS	DISS. SOLIDS	PH	SULPHATE AS SO_4	KJELDAHL NITROGEN AS N	AMMONIA AS N	NITRATES AS N
T28-41	10	300	1,600	7,400	9.5	114	9,500	200	375
T28-42	5	140	65	775	8.6	29	350	20	25
T28-43	4	55	25	675	8.2	45	190	6	17

DISCUSSION OF RESULTS

The discharge of mother liquor to the sewer must cease. Though there is a low flow, 1 - 2 Imperial gallons per minute, the concentrations of contaminants make this an extremely powerful waste stream. The waste loadings from this source in a 24-hour production period are 275 lbs. of Kjeldahl nitrogen, 50 lbs. of suspended solids, 205 lbs. dissolved solids,

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7 lbs. of free ammonia, 50 lbs. of nitrates.

The other waste discharge from this plant is in the main sewer discharge, a volume of 10 Imperial gallons per minute. This flow contains high concentrations of chemical oxygen demand, suspended solids and dissolved solids, Kjeldahl nitrogen, free ammonia nitrates and sulphates.

The standard of housekeeping at this plant requires upgrading as evidenced by the substantial quantities of product seen on the plant floor during the survey.

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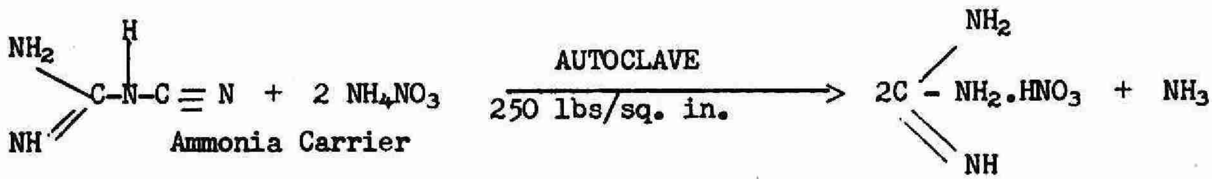
GUANIDINE NITRATE PLANT

Raw Materials and Products

Dicyandiamide and ammonium nitrate are reacted together under conditions of high temperature and pressure to form guanidine nitrate. Ammonia is used as a carrier for the ammonium nitrate.

Process

The reaction equation is:



dicyandiamide   ammonium nitrate   guanidine nitrate

Dicyandiamide, ammonium nitrate and liquid ammonia are mixed together and passed into an autoclave at 250 lbs. sq. in. pressure and a temperature of 600°C. Guanidine nitrate is formed and the ammonia, used as a carrier for the ammonium nitrate, is also present. When this mixture leaves the autoclave, the ammonia "flashes off", into a closed condensor system. The ammonia is condensed, cooled and sent to storage tanks for use again in the initial step of the process. When the ammonia has "flashed off", the dry guanidine nitrate is bagged.

The plant operates on a batch basis manufacturing eight 9,000 lbs. batches of guanidine nitrate. The plant operates 24 hours/day and 7 days/week.

The guanidine nitrate manufactured is used as a raw material in the manufacture of picrite. Some is also sold as guanidine nitrate.

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Sources of Wastes and Disposal

A considerable volume of cooling water is used at this plant. Water condensors, compressors and pumps all use cooling water. The pumps also use water as a sealant. All cooling water is recirculated from a plant cooling tower, however, there is an overflow pipe from this system to the sewer. There is a constant overflow from the system to sewer which was estimated at 50 Igpm on the day of the survey. The volume of cooling water overflow varies, with much less of an overflow during the winter months. This sewer discharges to Thompson's Creek.

This is the only flow of wastewater from the guanidine nitrate plant.

There was, however, a considerable spillage of guanidine nitrate in and around the plant. The guanidine nitrate is transported to the picrite plant in box cars and there was a trail of product between the two plants. This would be washed to roadside ditches during rainy weather and eventually flow to Thompson's Creek.

Sanpling and Analysis

A grab sample of the cooling water overflow was obtained:

LAB. NO.	FLOW	PH	BOD	SOLIDS TOTAL	SOLIDS SUSP.	SOLIDS DISS.	TOTAL KJELDAHL	FREE AMMONIA	NO_3^-	NO_2^-	COD	CHLORIDE	SULPHATE
T28-33	50	9.0	10	300	15	285	11	4	5.9	2.0	25	34	71

All concentrations except pH are in ppm.

The flow rate is in gallons per minute.

DISCUSSION OF RESULTS

There are no adverse comments on this cooling water flow. As discussed above, housekeeping must be improved at this plant to ensure that nitrogen rich guanidine nitrate is not washed to adjacent ditches.

PICRITE PLANT

Raw Materials and Product

Guanidine nitrate and 93% sulphuric acid are mixed together forming picrite.

Process

The reaction equation is:

$$\underset{\text{Guanidine Nitrate}}{\overset{NH_2}{\underset{NH}{C}} - NH_2.HNO_3} \xrightarrow[-\ H_2O]{93\%\ H_2SO_4} \underset{\text{Picrite}}{\overset{HN_2}{\underset{NH}{C}} - NH.NO_2} + H_2O$$

Guanidine nitrate and 93% sulphuric acid are mixed by constant recirculation through batteries of stainless steel pipes. The reaction is exothermic and there is a constant flow of cooling water over the surfaces of the piping system.

The discharge from the reaction complex is diluted with water and mother liquor, which has been recirculated from the final filtering process. This dilutes the solution from an acidity of 65% to one of 17.5%. The solution is vacuum cooled to 12°C and crude picrite is filtered out. The waste acid is pumped to the dicyandiamide plant for neutralization.

The crude picrite is redissolved in water and recirculated mother liquor then recrystallized using an air cooled spray crystallizer. The purified picrite slurry now undergoes further dilution with water and mother liquor until the slurry contains 6% picrite by weight.

The 6% slurry passes through a final filtration process. The mother liquor is recirculated to be used as a dilutant in the process while the picrite cake is vacuum dried and packed into boxes.

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This process is continuous and operates 24 hours per day, seven days per week. Picrite is not used in any further plant processes so all picrite manufactured is sold.

Source of Liquid Wastes and Disposal

All waste waters from the picrite plant flow to sewers that discharge to Thompson's Creek, which, in turn, empties into the Welland River about one mile downstream of the Cyanamid plant.

The reactor cooling water is recirculated. There is, however, an overflow of cooling water from the reservoir underneath the batteries of mixing pipes. This cooling water is discharged to sewer.

Vacuum coolers are used to cool the crude picrite solution to 12°C. The vacuum is caused by a fast flow of steam and water and there is a considerable discharge of water and steam condensate from the three coolers. All three coolers discharge to a common sump inside the plant.

There is a pit below the redissolving tank whose contents are pumped to the sewer three times a shift. This effluent contains picrite slurry overflows, as well as discharges from water cooled pumps and pump seals.

A considerable volume of cooling water is used on the filter machines. These wastes, along with all other cooling water discharges flow to a common sump inside the plant.

Sampling and Analysis

Two composite samples of the total plant effluent were taken from the sump inside theplant. One was composited from 10:00 a.m. - 2:00 p.m., the other from 2:00 p.m. - 10:00 p.m. Grab samples of the reactor cooling water and the Oliver filter wash-up were obtained.

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LAB.NO.	FLOW	BOD	Solids TOTAL	Solids SUSP	Solids DISS.	Nitrogen TOTAL KJELDAHL	Nitrogen FREE AMMONIA	Nitrogen NO_3^-	Nitrogen NO_2^-	COD	CHLORIDE	SULPHATE	PH
T28-22	300	6.0	810	15	795	160	13	10.6	0.31	55	-	-	7.6
T28-35	300	6.0	1480	20	1460	130	0.38	10	0.30	45	36	265	7.4
T28-21	25	6.5	300	10	290	65	13	16.6	3.4	35	-	-	8.6
T28-36	-	5.0	12480	8050	4430	480	60	20	0.39	80	50	750	7.3

All results are recorded in ppm. Flow rates are gallons/minute.

Samples T28-22, T28-35 represent the total plant effluent to the sewer
Sample T28-21 represents the cooling water overflow from the mixing coils
Sample T28-36 represents wash waters from the Oliver Filter

DISCUSSION OF RESULTS

The main problems are high concentrations of Kjeldahl nitrogen, nitrates, dissolved solids and chemical oxygen demand. The daily waste loading from the plant is 580 lbs. Kjeldahl nitrogen, 3,640 lbs. dissolved solids, 100 lbs. chemical oxygen demand and 105 lbs. of nitrate for a 24-hour period.

Two obvious sources of contaminated wastes are wash waters from the Oliver filter and water pumped from the pit in the manufacturing area. Both these should be retained and recirculated into the manufacturing process.

The other main sources of wastes are discharges from the vacuum coolers.

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NEUTRALIZATION PLANT

At the neutralization plant, waste acid (15% sulphuric) from the picrite plant is neutralized with calcium carbonate slurry produced at the dicyandiamide plant. The neutralized slurry is then pumped to the sludge ponds.

Sources of Liquid Wastes

The plant is served by a sewer draining into Thompson's Creek. Spillages in the plant drain directly to this sewer. The flow in the sewer has been estimated at 10 gpm although this is variable.

Sampling and Analytical Results.

Sample No.	Description		Flow
T28-60	Sewer to Thompson's Creek	Comp. 9:30 am-3:30pm	10 gpm
T28-61	Sewer to Thompson's Creek	Comp. 4:30 pm-10:00 pm	10 gpm
T28-62	Acid Waste to Plant	Grab 11:00am	60 gpm
T28-63	Calcium Carbonate Waste to Plant	Grab 11:10am	
T28-64	Neutralized Effluent to Ponds	Grab 11:20am	300 gpm

SAMPLE NO.	SUSP. SOLIDS	DISS. SOLIDS	PH	AMMONIA NITROGEN AS N	KJELDAHL NITROGEN AS N	COD	SULPHATES AS SO_4	CARBONATES AS CO_3	CALCIUM AS CA
T28-60	610	440	8.2	18	45	220	98	0	-
T28-61	1,060	440	7.8	12.5	38	480	106	0	68
T28-62	CLEAR	-	0.2	-	-	100	6,250	0	244
T28-63	491,400	600	9.5	-	4,800	150,000	62	382	44
T28-64	230,400	4,600	6.7	400	2,700	62,000	1,625	0	688

DISCUSSION OF RESULTS

Samples T28-60, T28-61 are discharged to a sewer which leads to Thompson's Creek. This discharge is unacceptable to the OWRC as it contains high concentrations of suspended solids, Kjeldahl nitrogen and free ammonia. Waste loadings are shown below. The Company should find methods of eliminating the suspended solids dicharge. The problem of free ammonia and Kjeldahl nitrogen will be discussed elsewhere in the report.

Contaminants	Waste Loadings Over 24-hour period in lbs.
Free Ammonia	2.0
Total Kjeldahl Nitrogen	5.0
Suspended solids	120.0

Discharge from Active Settling Pond to Thompson's Creek

At the neutralization plant, calcium carbonate slurry from the dicyandiamide plant is neutralized by waste sulphuric acid from the picrite plant. The neutralized slurry is then pumped to sludge ponds where solids are settled. There is an overflow from these sludge ponds to Thompson's Creek estimated at 300 Imperial gallons per minute.

Analytical Results

Two grab samples of the overflow from No. 9 settling pond were obtained. The results are as follows:

SAMPLE NO.	BOD	SOLIDS			PH	NITROGEN AS N				COD
		TOTAL	SUSP.	DISS.		TOTAL KJELDAHL	FREE AMMONIA	NITRATE	NITRITE	
T28-20	1.2	4,980	5	4,975	7.9	1,500	936	87	3.4	105
T28-44	6.5	4,920	120	4,800	7.7	2,100	280	80	6.0	85

	CHLORIDES	SULPHATES
T28-20	THESE ANALYSES NOT ASKED FOR.	
T28-44	129	1,690

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There is a considerable waste loading from this waste flow.

Contaminants	Waste Loadings in lbs/24-hour period
Suspended Solids	190
Dissolved Solids	19,850
Free Ammonia	3,180
Nitrates	1,570
Sulphates	7,120
Nitrite	100
Chlorides	425
Kjeldahl Nitrogen	7,740
Chemical Oxygen Demand	440

The waste loadings are calculated on the assumption that there is a continuous 300 Imperial gallons per minute overflow from the sludge pond.

3-AMINO 1, 2, 3, TRIAZOL PLANT

Raw Materials

Guanidine nitrate, ammonium sulphate, carbon dioxide and formic acid react together to give 3-Amino 1, 2, 3, Triazol.

Plant Process

Ammonium sulphate and a 15% nitroguanidine slurry are reacted in an autoclave with water and hydrogen in the presence of a nickel/chromium catalyst to form amino guanidine sulphate. The catalyst is removed by filtration and carbon dioxide is bubbled through the remaining liquid. Amino guanidine bicarbonate is precipitated and filtered. The mother liquor flows to a holding tank and is discharged to a sewer.

The amino guanidine bicarbonate cake is dissolved in formic acid to form amino guanidine formate. The formate is subjected to conditions of high temperature and pressure to form the finished product 3-Amino 1, 2, 3, Triazol.

The plant operates 24 hours/day, 7 days/week, and produces approximately 100,000 lbs. of 3-Amino 1, 2, 3, Triazol, a defoliant, each month. All the 3-Amino 1, 2, 3, Triazol manufactured is sold as such.

Sources of Liquid Wastes and Disposal

There are two waste discharges from this plant:

(1) Cooling water, a volume estimated at 80 Imperial gallons per minute, is discharged to a sewer which leads to Thompson's Creek.

(b) The filtrate left after filtration of the amino guanidine bicarbonate is held in a storage tank then discharged to a sewer

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which discharges to Thompson's Creek. The daily volume of this discharge is 9,000 Imperial gallons.

Sampling and Analysis

A grab sample, T28-26, was obtained of the cooling water discharge. Composite samples of the filtrate were taken over a 12-hour period. These were numbered T28-25 and T28-34.

SAMPLE NO.	FLOW	BOD	SOLIDS TOTAL	SOLIDS SUSP.	SOLIDS DISS.	PH	NITROGEN TOTAL KJEL.	NITROGEN FREE AMMONIA	NITROGEN NO_3	NITROGEN NO_2	COD	CHLORIDE	SULPHATE
T28-25	9,000 GPD	55	22,680	690	21,990	7.8	5,500	5,000	0.13	0.03	660	-	-
T28-34	9,000 GPD	**	23,540	220	23,320	7.8	5,800	5,250	0.50	0.02	720	290	13,300
T28-26	80 GPM	3.5	410	25	285	8.7	215	170	0.59	0.31	30	-	-

** INTERFERENCE INHIBITED ANALYSIS

DISCUSSION OF RESULTS

The mother liquor discharge to the sewer must be stopped. There is a considerable waste loading from this source.

Contaminants	Waste Loadings in lbs/24 hr.
Dissolved Solids	2,000
Kjeldahl Nitrogen	500
Free Ammonia	560
Chemical Oxygen Demand	60
Sulphates	1,200

This waste flow was not analysed for nickel. However, the plant is suspected of being one of the sources of the nickel found in Thompson's Creek. Discharges from this plant should be analysed for nickel content.

The cooling water flow has obviously been contaminated in the production process and should not be discharged without pretreatment. Daily waste loading of free ammonia and Kjeldahl nitrogen from this source are 230 lbs. in each case.

AUROFAC PLANT

Production

Six thousand and six hundred (6,600) lbs. of Aureomycin mash, an animal feed supplement are produced monthly. The plant normally operates 5 days per week, 24 hours per day.

Plant Processes

Water, corn steep liquor, calcium carbonate, corn starch and lard oil are fed to two small seed fermenters. The cultures are transferred to two process fermenters to which water, corn steep liquor, calcium carbonate, corn starch, monopotassium phosphate, ammonium sulphate, ammonium chloride, manganese sulphate, lard oil and corn flour are added. Two batches per week are produced.

After fermentation, the slurry is filtered using a diatomaceous earth precoat. The cake is air-dried using steam heat, ground, blended with other additives such as sulphur drugs, and bagged for sale. The filter liquor is sent to refermenters to reduce the organic content. The refermented liquor is disposed of by pumping to one of the non-active sludge ponds.

Sources of Liquid Wastes and Disposal

Some recirculated cooling water is used on air compressors and the after-coolers to remove oil and moisture from the fermenters. The major waste stream, refermented mash liquor, is pumped for disposal to a non-active sludge pond.

Sampling and Analysis

Sample No.	Description	Flow (gpd)
T28-10	Aurofac Plant waste to sewer - Grab sample	300

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SAMPLE NO.	BOD_5	SUSP. SOLIDS	DISS. SOLIDS	PH	COD	KJELDAHL NITROGEN AS N	NITRATE AS N	NITRITE AS N
T28-10	65	30	910	7.7	70	4.8	8.4	3.1

DISCUSSION OF RESULTS

This waste flow contains excessive concentrations of BOD_5, COD, and Dissolved Solids and should not be discharged to the sewer without treatment. Waste loadings have not been calculated as the flow of wastes is so small i.e. 300 Imperial gallons each day.

PHOSPHINE AND ORGANIC DERIVATIVES PILOT PLANT

(a) Phosphine

Raw Materials

The raw materials at this plant are:

(1) yellow phosphorous

(2) sodium hypochlorite (12% solution)

(3) steam

Yellow phosphorous is melted using hot water. The molten phosphorous is moved by water displacement to a graphite-lined phosphine generator where it is reacted with steam and sodium hypochlorite to form phosphine gas and the by-products, water, sodium chloride and disodium phosphate. The phosphine gas containing hydrogen, some water vapour and nitrogen, to maintain a positive pressure in the system, is liquified at 800 lbs/sq.in. and -60°F. The non-condensables (hydrogen and nitrogen) are scrubbed in a sodium hypochlorite-water scrubber. The scrubbing solution is recirculated with the overflow going to waste.

Design capacity of the plant is 200,000 lbs. of phosphine gas per year.

(b) Organic Derivatives

The organic derivatives plant can produce a variety of organic phosphine or phosphorous based chemicals. The general process used involves reacting the chemicals, crystallization of the product, filtration, and refining of the product by dissolving in a solvent followed by recrystallization. On the day of the survey, TRIS (2-carbamylethyl) phosphine oxide was being produced using acrylamide and potassium hydroxide.

Sources of Liquid Wastes and Disposal

The liquid remaining in the phosphine generator containing disodium

phosphate, sodium chloride and water, the waste gas scrubbing solution containing disodium phosphate and water, and the process waste from the organic derivatives plant treated with sodium hypochlorite and disodium phosphate, and other contaminants depending on the product being produced are discharged by gravity to a sump where lime for neutralization is added before pumping to No. 6 Sludge Pond (in-active).

Indirect cooling water, used throughout the plant, and condensate from steam heating coils is discharged to a sewer emptying into Thompson's Creek.

Any spills from the reaction section of the organic derivatives plant are contained in a curbed area and directed to a wooden, baffled box overflowing to a ditch.

Sampling and Analysis

Sample No.	Description		Flow
T28-11	Waste flow to Sewer at Wooden Box	Comp. 10:00am - 2:00pm	1 GPM
T28-12	Waste flow to Sewer at Wooden Box	Comp. 2:00pm -10:00pm	
T28-13	Sump (to sludge pond)	Grab.	250 GPH

SAMPLE NO.	BOD_5	SUSP. SOLIDS	DISS. SOLIDS	PH	COD	PHOSPHORUS AS P	KJELDAHL NITROGEN AS N	AMMONIA AS N	NITRATE AS N
T28-11	3	10	980	7.9	160	15	16	13	11
T28-12	2.5	10	980	7.9	170	17	14	7.5	0.4
T28-13	-	95	1,075	6.3	45	300	2.8	1.5	1.2

DISCUSSION OF RESULTS

The wastewater overflow from the wooden box, although only 1,440 gallons per day, should not be discharged to the ditch as analysis showed high con-

centrations of Kjeldahl nitrogen, free ammonia, nitrates, phosphorous, dissolved solids and chemical oxygen demand in this waste flow.

There was no flow of cooling water or condensate from the steam heating coils during the duration of this survey.

No waste loadings have been calculated due to the small flow of wastes involved.

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XANTHATE PLANT

Raw Materials and Products

Xanthates are manufactured from carbon disulphide, sodium or potassium hydroxide and one of four alcohols, isobutyl, isopropyl, secondary butyl or amyl alcohol. There are four xanthate end-products depending on the alcohol used. Xanthates are used in the mining industry to separate minerals from crude ore.

Process

The reaction equation is:

$$\underbrace{CS_2 + \underset{\text{Flake}}{NaOH} + R.OH}_{\text{Naphthalene Carrier}} \xrightarrow[\text{Reaction}]{\text{Exothermic}} \underset{\substack{\text{Xanthate}\\ 3,500\text{ lbs.}}}{R-O-\overset{\overset{S}{\|}}{C}-S-Na} + \underset{1,000\text{ lbs.}}{H_2O}$$

R = either isobutyl, isoproply, secondary butyl or amyl grouping. Naphthalene is used as a carrier only and plays no chemical role in the reaction processes.

Since this reaction is exothermic, the reaction vessel is cooled. A 50% ethylene glycol solution is used. The cooling system is a closed one with no discharge to the sewer.

The naphthalene used as a carrier "flashes off" from the reaction vessel and is collected, with the water also generated in the reaction, in the naphthalene holding tank. The naphthalene/water mixture separates into a two-phase system and the naphthalene is drawn off for re-use.

The end product, xanthate, is vacuum dried at $60^{o}C$-$90^{o}C$, the temp - erature varying with the type of xanthate being produced. After drying the xanthate is cooled, using recirculating plant cooling water, and bagged.

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This plant operates on a batch basis. There are four batches a day producing 3,500 lbs. xanthate/batch.

All cooling water used is recirculated to the plant cooling tower. There are no sewer discharges of cooling water.

Sources of Liquid Wastes and Disposal

The water phase from the naphthalene holding tank is discharged to a sewer which discharges to Thompson's Creek. Approximately 100 gallons/ batch i.e. 400 gallons per day are discharged to the sewer.

Steam condensate from the vacuum drier, is collected in the naphthalene cutting tank. Some naphthalene is also carried over. There is, again, a separation of naphthalene and water, the water being sewered and the naphthalene drawn off for re-use. The volume of water being sewered was estimated at 2,000 gpd.

Sampling and Analysis

Grab samples of the discharges from the naphthalene holding and cutting tanks were obtained.

NAPHTHALENE HOLDING TANK

LAB NO.	VOL.	BOD	SOLIDS TOTAL	SOLIDS SUSP.	SOLIDS DISS.	PH	TOTAL KJELDAHL	FREE AMMONIA	NO_3^-	NO_2^-	ETHER SOLUBLES	NI	COD
T28-23	400	> 18,000	160	5	155	7.5	0.77	0.50	0.07	0.01	23	0.0	750,000

NAPHTHALENE CUTTING TANK

LAB NO.	VOL.	BOD	SOLIDS TOTAL	SOLIDS SUSP.	SOLIDS DISS.	PH	TOTAL KJELDAHL	FREE AMMONIA	NO_3^-	NO_2^-	ETHER SOLUBLES	NI	COD
T28-24	2,000	34,000	15	10	5	85	8.5	8.0	<0.01	0.04	11	0.25	36,000

DISCUSSION OF RESULTS

Both waste flows are extremely high in BOD_5 and COD, and should not be discharged to a watercourse without treatment. The waste loadings from this plant are as follows:

Waste Source	Contaminant	Loadings in lbs/24-hour period
Naphthalene Holding Tank	Bio-chemical Oxygen Demand	360
	Chemical Oxygen Demand	15,000
Naphthalene Cutting Tank	Bio-chemical Oxygen Demand	140
	Chemical Oxygen Demand	145

Total waste loadings from the xanthate plant were:

BOD_5	500
COD	15,145

N.B. Since this report was prepared, proposals have been received from the Company to change the xanthate manufacturing process. The basic change would be the cessation of the use of naphthalene as "carrier" in the reaction vessels and would eliminate the naphthalene holding tank and cutting tank discharges to sewer.

Discussions with the Company have revealed a daily loss of approximately 45 lbs. of finished product xanthate to the sewer. A reduction of these losses is essential, as xanthates have been shown to be extremely toxic to fish life, even in low concentrations.

MAIN STEAM PLANT

Raw water from the Welland River (or treated water from the water treatment plant) is treated chemically and heated to form steam.

Process

Boiler waters receive the following treatment.

(a) The water is first softened by ion exchange and then treated with E.D.T.A. solution. There is no excess of E.D.T.A. in the treated water.

(b) Sodium sulphite is added to remove any traces of dissolved oxygen. There is an excess of 30 - 50 ppm sodium sulphite in the treated effluent.

(c) An anti-foam and sludge conditioner named "liqui-treat" is drip added at a rate of 9 lbs/day. "Liqui-treat" is supplied by Betz Laboratories who have been approached for formulation information.

(d) The sodium zeolite resin is regenerated twice daily using sodium chloride. Two thousand (2,000) lbs. of rock sodium chloride are used on each regeneration with a subsequent sewer discharge containing calcium and magnesium chlorides.

Sources of Liquid Wastes

There is a constant blowdown to the 36" sewer of 125 Imperial gallons per minute.

Sampling and Analysis

Two grab samples of the blowdown to the sewer were obtained at 12:00 a.m. and 5:30 p.m. and composited.

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			SOLIDS							NITROGEN				
LAB.NO.	FLOW GPM	BOD	TOTAL	SUSP.	DISS.	COD	$\overline{CL}$	$\overline{SO_4}$	PH	TOTAL KJELDAHL	FREE AMMONIA	NITRATE	NITRITE	CR.
T28-18	125	28	3,640	5	3,635	180	694	1,118	11.7	6.6	1.0	50	9.4	0.02

Carbonate alkalinity was 220 ppm.

DISCUSSION OF RESULTS

This flow contains high concentrations of chlorides, 694 ppm, and sulphates, 1,118 ppm, and has a high COD concentration. Waste loadings from this source are as follows:

Contaminants	Discharge/24-hour period in lbs.
Dissolved Solids	6,025
Sulphates	2,040
Chlorides	1,090
COD	275
Nitrate s	360

The pH of this discharge is also high.

AMMONIA-UREA COOLING TOWER

This plant supplies cooling water to the ammonia/urea manufacturing complex.

Process

There is a constant recirculation through the plant of 25,000 U.S. gallons per minute. The following additives are used:

(a) "Dianodic 193C", a chromate/phosphate/zinc corrosion inhibitor supplied by Betz Laboratories. One hundred and fifty (150) lbs. of "Dianodic 193C" are added daily.

(b) "Dispersant #405" - 32 lbs/day are added to prevent build-up of Fe_2O_3 in the recirculating water. It is supplied by Betz Laboratories.

(c) 1400 lbs. of 97% sulphuric acid to keep the pH of recirculating waters at 6.4. This pH ensures that all chemicals added stay in solution.

(d) 150 lbs. of chlorine/day to protect the wood in the cooling tower.

(3) 50 lbs/month of CYTOX#3522 - a biocide supplied by American Cyanamid.

The constant overflow from the cooling tower flows to the 36" sewer and amounts to 250 gpm.

Sampling and Analysis

Two grab samples of the overflow to the 36" sewer were taken at 12:00 a.m. and 5:30 p.m. and composited.

			SOLIDS				NITROGEN										
LAB.NO.	FLOW GPM	BOD	TOTAL	SUSP.	DISS.	PH	TOTAL KJELDAHL	FREE AMMONIA	NITRATE	NITRITE	P	COD	CHROMIUM	ZINC	$SO_4^{=}$	CL^{-}
T28-19	250	6.0	1,000	5	995	7.2	53	44	11	0.36	5.4	55	20.2	3.0	410	134

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DISCUSSION OF RESULTS

The main problem associated with this discharge is the presence of high concentrations of the heavy metals chromium and zinc. The metals are present in the corrosion inhibitor "Dianodic 193C" which is added to the cooling tower water at a rate of 150 lbs/day. The daily discharges of these metals from the plant is 75 lbs. of chromium and 11 lbs. of zinc.

Heavy metals do not break down naturally. They are retained by and accumulate in the environment. The quantities of chromium and zinc discharged in this waste stream must be regarded as serious. The Company should investigate the substitution of alternative corrosion inhibitors or consider treatment of this waste flow to remove and recover these heavy metals.

The cooling water overflow to the sewer also contains high concentrations of dissolved solids, Kjeldahl nitrogen, free ammonia, sulphates, chlorides, and chemical oxygen demand. The waste loadings from the plant are as follows:

Contaminants	Loadings in lbs/24-hour period
Dissolved Solids	2,560
Kjeldahl Nitrogen	140
Free ammonia	160
Nitrates	115
Chemical Oxygen Demand	100
Chromium	75
Zinc	11
Sulphates	1,320
Chlorides	100

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WATER TREATMENT PLANT

The major source of water supply to the Cyanamid complex is the Welland River. A small portion of the water drawn from the river is used untreated as cooling water, however, most of the water is treated prior to use.

Treatment consists of the addition of ferrous sulphate, calcium carbonate and oxygen to the raw water. The addition of these chemicals produces a ferric hydroxide floc which settles to form a sludge bed. The sludge bed acts as a filter on the river water which is naturally high in suspended solids. Used ferric chloride sludge is automatically pumped to a settling basin (accelator) where solids settle. The supernatant liquid from the pond overflows to Thompson's Creek.

There was no overflow from the accelator pond at the time of this survey, however, samples of supernatant liquor were taken beside the overflow.

Sampling and Analysis

Sample No.	pH	BOD_5	SOLIDS Total	Susp.	Diss.	NITROGEN Kjel.	Free Amm.	NO_3	NO_2	PO_4	COD
T28-14	9.3	6.5	650	175	475	4.3	0.5	0.5	0.55	5.1	120

The accelator pond is not providing satisfactory sludge settling and the supernatant liquor should not be allowed to overflow to Thompson's Creek.

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Regional Engineer,
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BIOLOGICAL REPORT

INTRODUCTION

In June of 1970, a request was received from Mr. R. Stewart of the Division of Industrial Wastes for toxicity data on the two effluent streams originating from the Cyanamid of Canada, Limited plant near Welland. On July 9, two samples of effluent were received. One was identified as "Miller's Creek" and the other was identified as "Main Sewer to Welland River". The creek on the plant property is known locally as Miller's Creek; however, the Gazetteer of Canada, Ontario 1962 ed. (1) identifies this creek as Thompson's Creek.

Fertilizers, base metal milling and processing chemicals and antibiotics are the major products manufactured at this plant. Table 1 indicates the major effluent components, concentrations and loadings.

Table 1. Waste components and loadings

	Main Mill Sewer		Thompson's Creek	
IGPM	500		5,500	
IGPD	720,000		7,920,000	
Component	Conc. (mg/L)	Load (#/day)	Conc. (mg/L)	Load (#/day)
Free ammonia	750	4,860	50	3,564
BOD_5	13	84	30	2,140
Dissolved Solids	8,575	56,500	795	56,230
Chloride	2,939	1,940	125	8,553
COD	610	61,000	90	7,036
Total Kjeldahl Nitrogen	1,050	105,000	200	14,256
Urea	300	30,000	150	10,700
Cyanide			0.3	21.4

METHODS

The purpose of the toxicity test is to evaluate the TLm of the effluent. The TLm is defined as the tolerance limit median in a specified time "t". A 96-hour TLm of 13.5% v/v represents the concentration at which half of the test organisms will survive a 96-hour exposure. Working from the TLm concentration a dilution volume (D.V.) and safe concentrations (Qs) can be calculated. The dilution volume is defined as that amount of receiving water necessary to dilute the effluent to a specified TLm concentration. The safe concentration is that concentration of effluent producing neither lethal nor sublethal effects and which will not deplete the assimilative capacity of the receiving water to the detriment of any other water use. The dilution volume (D.V.) is calculated according to the formula:

$$\text{D.V.} = \frac{100 - \text{TLm}(\%)}{\text{TLm}(\%)} \times \text{Effluent Flow (gpm)}$$

The safe concentration (Qs) is calculated from the formula Qs = D.V. X Fa where Fa equals an application factor based upon the amount and character of the waste. In the absence of specific information pertaining to chronic or sublethal effects on the biota this application factor must be selected somewhat arbitrarily. In such cases it has become accepted practice amongst toxicity biologists to establish Fa as 1/10 or 1/100 depending on the pattern of mortality exhibited by the test organisms during the toxicity bioassay and on the known chemical and physical characteristics of the waste components.

Initially, a range test was undertaken on each waste utilizing a series of widely-spaced dilutions to determine the magnitude of toxicity present in the materials. For this purpose, two-litre quantities of the

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waste were prepared in the following concentrations: 0.1% v/v, 1.0% v/v, 10% v/v and 100% v/v. The range test was run for 48 hours using the common fathead minnow, Pimephales promelas.

Following the range tests a series of full-scale bioassays were prepared as outlined in "Standard Methods for the Examination of Water and Wastewater, 12th ed." The full-scale bioassay provided TLm concentrations as previously described.

RESULTS

The acute toxicity bioassay showed that both waste streams were toxic to fish with the main mill sewer approximately 10 times more toxic than Thompson's Creek. The TLm concentrations were calculated through the graphical interpolation technique and were found to be as follows:

Duration of Exposure	Effluent Source - TLm Concentrations Main Mill Sewer	Thompson's Creek
4 hours	2.4% v/v	41% v/v
24 hours	2.0% v/v	29% v/v
48 hours	1.8% v/v	25% v/v
96 hours	1.3% v/v	13% v/v

The dilution volume (D.V.) for the main mill sewer and Thompson's Creek were calculated to be 40,150 IGPM and 35,200 IGPM respectively. Using an application factor (Fa) of 100 for each effluent source it was calculated that a total of 7.48 million IGPM of receiving water would be required to dilute the waste to a safe concentration (Qs). The reason for the application factor of 100 can be explained as follows. A log/log plot of TLm concentration

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vs. time indicate that both effluents showed a substantial increase in toxicity between 48 hours and 96 hours. The increase in toxicity is thought to result from the conversion of urea to ammonia and that two or three days after discharge the waste would become more toxic than when first discharged.

Table 1 shows the results of a series of chemical analyses performed on the two waste samples. With the exception of urea which was not analysed the table of analyses accounts for 62.4% and 59.5% of the dissolved solid in the main mill sewer and Thompson's Creek respectively.Of the chemical components measured ammonia is likely to be the most toxic agent.

DISCUSSION

By definition the TLm value is that concentration of a substance in water which will allow 50% of the test animals to survive in a specified time. The dilution volume is that amount of receiving water required to dilute the effluent to a specified TLm concentration. To achieve a safe concentration an application factor is used based on the amount and character of the waste and receiving water and the shape of the time/toxicity plot (appendix I). The waste showed an increase in toxicity with increasing exposure. Such an increase necessitates the use of a large application factor.

Depending on the requirements of the Ontario Hydro Electric Commission, the Welland River is subject to periods of extremely low flow. These low flow conditions have been commented upon previously by Johnson, 1964 (2). Johnson emphasises the toxic nature of the Cyanamid waste and the subsequent debilitating effects on the river fauna. The results of these bioassays indicate that significant improvements would not have taken place since 1964.

Water quality data collected by the OWRC in 1966(3) indicated that the river at the Montrose bridge had the following characteristics:

T °C	D.O. % Sat.	Bicarb. Alk. ($CaCO_3$)mg/L	pH	NH_3 mg/l	CO_2 Assumed mg/l	Estimated safe NH_3 Conc.
8.0	67	100	8.3	9.8	5	9.4

McKee and Wolfe (4) indicate that, "In the U.S. waters that ordinarily support good fish fauna ... 95 percent have less than 5 mg/l of free carbon dioxide". Using these data and the predictive model of Lloyd (5) the maximum safe concentration of ammonia in the river was calculated to be 9.4 mg/L. This concentration is one which will not produce mortailty in fish over an extended period of exposure. It does not take into consideration sublethal effects such as reduced growth, reduced swimming performance and increased susceptibility to disease all of which are known to occur in fish exposed to concentrations of ammonia much less than 9.4 mg/L (6). Also, the safe concentration of 9.4 mg/L doesn't take into consideration the presence of other pollutants. Phenol will reduce the fishes resistance to ammonia poisoning (5). Appendix III contains a more complete discussion of ammonia and its toxicity.

Quite apart from the toxicity of ammonia to aquatic life,discharges of nitrogenous compounds are undesirable because of the resulting eutrophication problems. The manifestation of continuing nutrient input to receiving waters are well known and will not be discussed here in detail. However, obvious examples are the proliferation of planktonic and filamentous forms of algae which severely lower the aesthetic quality of the water and which tend to create low oxygen conditions at the time of their decay. The problem may be critical beneath the winter ice coverings particularly where extensive stands of rooted macrophytes are also found.

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CONCLUSION

The Welland River cannot be considered as an adequate source of dilution water to assimilate the plant waste in its present form. It is strongly urged that immediate and determined efforts be made to find alternative methods of disposal with particular attention being paid to urea and ammonia. No improvement can be expected in the biological condition of the river until such measures are completed. Considerable attention has been devoted to the Welland River, which for purposes of this study has been considered the receiving water for the Cyanamid waste, but the implication to Thompson's Creek cannot be disregarded. Rehabilitation of the creek would not be expected even when water quality requirements for the Welland River have been met. Undoubtedly improvements in the river are of prime importance but waste processing modifications should be designed with the final objective of also eliminating pollution of Thompson's Creek.

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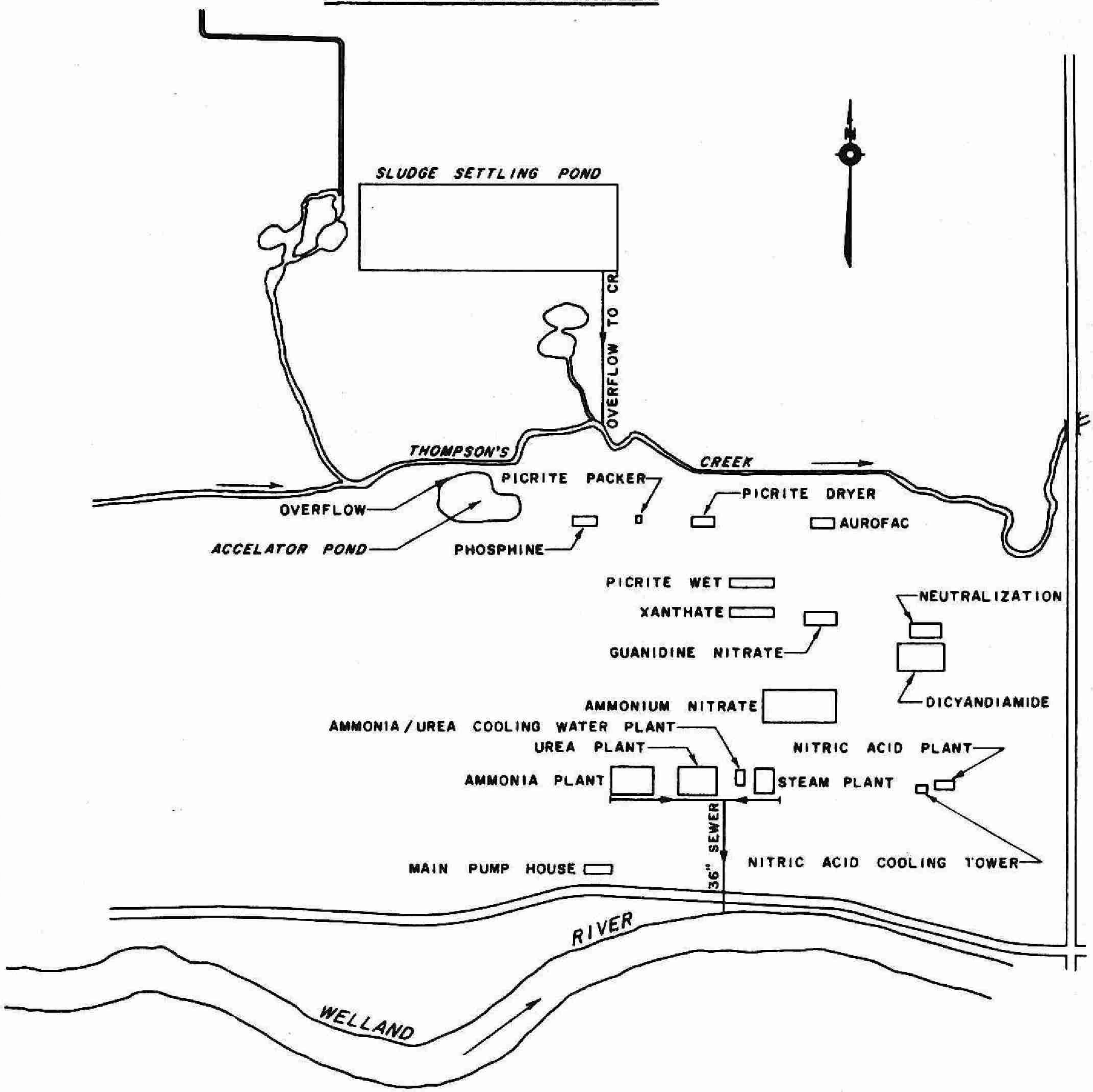
LAYOUT OF CYANAMID COMPLEX



NOTE

AMMONIA, UREA, STEAM AND AMMONIA / UREA COOLING WATER PLANTS DISCHARGE TO THE WELLAND RIVER VIA 36"Ø SEWER. ALL OTHER PLANTS DISCHARGE TO THOMPSON'S CREEK.

ONTARIO WATER RESOURCES COMMISSION	
CYANAMID OF CANADA LIMITED WELLAND PLANT	
SCALE: 100 0 500 FEET	
DRAWN BY: A.R.S.	DATE: AUG., 1971
CHECKED BY:	DRAWING Nº: 71-72-IW

(9148)
MOE/WEL/REP/ANMA

